

AN INVESTIGATION OF ENERGY
RELATIONS AT THE SURFACE OF
ACTIVATED SILICA GEL

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY IN
THE UNIVERSITY OF MICHIGAN

BY
E. GRINNELL ALMY

1932

AN INVESTIGATION OF ENERGY
RELATIONS AT THE SURFACE OF
ACTIVATED SILICA GEL

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY IN
THE UNIVERSITY OF MICHIGAN

BY

E. GRINNELL ALMY

1932



The author wishes to express his appreciation to Professor F. E. Bartell for his constant interest and helpful advice in the direction of this investigation.

TABLE OF CONTENTS

I. RELATION OF WATER CONTENT AND TEMPERATURE OF ACTIVATION TO THE ACTIVITY OF SILICA GEL	
Introduction	1
Methods of Preparing Activated Silica	
Capillary Pore Structure of Silica Gel	
Survey of Literature on Water in Silica Gel	
Purpose of the Investigation	
Experimental	6
Apparatus	
Materials	
Results	
Discussion	10
Reproducibility of Activation	
Water in Activated Silica	
Similarity between Theories Concerning Bound Water	
Summary	15
II. ENERGIES OF IMMERSION OF SILICA IN PURE LIQUIDS	
Introduction	17
Free Surface Energy Changes	
Total Surface Energy Changes	
Purpose of the Investigation	
Experimental	20
Apparatus and Materials	
Results	
Discussion	25
Constancy of Ratios	
The Equation Connecting Adhesion Tension and Heat of Wetting	
Comparison of Observed and Calculated Ratios	
Summary	31



Digitized by the Internet Archive
in 2026

ACTIVATED SILICA GEL

The Relation of Activity to Water Content and Temperature of Activation

Introduction

Preparation of Activated Silica. Silica gel is usually prepared by treating sodium silicate of a suitable concentration with an acid such as hydrochloric acid, or with certain salts, such as ferric chloride, which are acid in reaction. The gelatinous mass thus formed is broken up, washed free from salts, and dried until the gel becomes hard and glassy in appearance. The water content at this stage will vary with the method of preparation but is nearly always well above five percent. Finally, the gel is heated to a moderately high temperature (150°C. to 400°C.), usually in a current of dry air. This process, known as activation, decreases still further the water content of the gel and increases greatly its adsorptive capacity. While the term "activated silica" is commonly applied to this product the term "silica gel" has often been used interchangeably with it. The latter term is also used to indicate not only activated gel but also gel which may contain much more water.

The preliminary drying of silica gel has been studied by van Bemmelen,¹ Zsigmondy² and others. This study is generally interpreted to show, (1) that the gel as it is first formed consists of an interlacing mass of silica threads the spaces between them being filled with capillary held water, and (2) that the preliminary drying drives out at least the major portion of this water. During the preliminary drying the gel shrinks in volume and, when ready for the final activation, is generally believed to consist of a mass of interlacing silica threads forming a multitude of micropores. The effective diameters of these pores have been estimated to be approximately $5\text{ m}\mu$.

Holmes³ has found that the shrinkage of the gel upon drying might be somewhat lessened if the gel, while still containing a relatively large percentage of water (60%) be kept at a high temperature (approaching 100°C.) and held in such a manner that water could not evaporate from the system. He believes that this process "sets" the framework so that upon subsequent drying the contraction is less than for gels not treated in this manner.

Kistler⁴ has succeeded in removing the water from silica gel with no attendant decrease of volume. This is accomplished by first displacing the water by an organic liquid miscible with it, and then by replacing the first

¹ Van Bemmelen: "Die Absorption," 205 (1910).

² Zsigmondy: "Kolloidchemie," 150 (1912).

³ Holmes: Ind. Eng. Chem., **17**, 280 (1925).

⁴ Kistler: Nature, **127**, 741 (1931).

organic liquid by another which has a very low critical temperature. If the gel is then heated in an autoclave to a temperature higher than the critical temperature of this liquid, and the pressure is slowly released, the organic liquid is removed but the total volume of gel is not appreciably altered. Gels thus prepared, called aerogels, have a very low apparent density, they retain the shape of the original gel and may under proper conditions be rehydrated to the original state. These gels, like those of van Bemmelen, always contain small amounts of residual water. In the case of the aerogels any attempt to remove this water results in a crumbling of the sample. This investigation has given good evidence that freshly prepared silica gels have a definite internal structure or framework. During the ordinary process of drying of such gels, they shrink to a small fraction of the original volume which indicates that the structural framework must collapse.

Structure of Activated Gel. Quite definite evidence of the existence of capillary pores in silica gel has also been obtained by Fells and Firth.¹ They found that when a gel prepared by the usual method is allowed to dry before the salt is washed out, long needles of sodium chloride grow out from the surface of the gel as it shrinks. As the drying and shrinking continue these needles break off and a new crop of finer needles appears. This evidence, they feel, indicates the existence of a capillary pore structure. The salt solution is squeezed out through the pores as the gel shrinks, the water evaporates, and the salt is deposited as needles. Further shrinkage contracts the pores and snaps off the first formed needles, whereupon a growth of finer needles is noticed as the gel continues to dry. They found that there was no difference between the finally obtained gels whether prepared by washing out the salt before sintering or after sintering.

Jones,² likewise, has obtained some evidence that silica gel must possess capillary pores. In an investigation upon adsorption from solution by silica of varying degrees of dispersivity, he found that silica gel adsorbed more of the solute than did less highly dispersed ground quartz. He concluded, however, from the shapes of the adsorption isotherms that the increased adsorptive capacity of the gel over that of the crystalline material could not be accounted for by the greater specific surface alone, but that fine capillary pores must exist within the gel which in some manner increase the adsorptive capacity.

It has been reported by Kyropoulos³ and others that silica gel shows no X-ray diffraction pattern and, therefore, that the silica constituting the framework of the structure is amorphous. Quite recently, however, Krejci and Ott⁴ obtained X-ray photographs of silica gel, that had never been treated at temperatures higher than 100°, and found the pattern of cristobalite to be distinctly visible. They believe that at least some crystalline nuclei are present in the gel.

¹ Fells and Firth: *J. Phys. Chem.*, **29**, 241 (1925).

² Jones: *J. Phys. Chem.*, **29**, 327 (1925).

³ Kyropoulos: *Z. anorg. allgem. Chem.*, **99**, 197 (1917).

⁴ Krejci and Ott: *J. Phys. Chem.*, **35**, 2061 (1931).

Patrick, Frazer, and Rush¹ have investigated the structure of silica gel as it varies with the temperature of activation. They studied the apparent densities, the adsorptive capacities for CCl_4 vapors, and the X-ray diffraction patterns of samples of gel that had been heated at successively increasing temperatures, each for a period of two hours. For temperatures up to 800°C . they found that the density and adsorptive capacity remained constant. As the temperature of activation was increased from 800° to 1000°C ., the density increased while the adsorptive capacity decreased to a minimum. This, it would seem, indicated a closing of capillary pores in the system, thereby decreasing the capillary volume as well as the effective surface area. None of these gels were found to exhibit diffraction patterns characteristic of crystalline silica. It was found necessary to heat the gel at 1100°C . for three days to produce sufficient crystallization to give visible diffraction patterns. Unfortunately the water content of the various samples was not determined.

The evidence obtained from the literature indicates that in activated silica we are dealing with the partially collapsed framework of a gel. The interstices between the interlacing mass of threads have become very small during the collapse so that they form microcapillary spaces. The effective radii of these pores are not the same throughout the gel but grade from a maximum, determined by the method of preparation, down to a radius of molecular dimensions. The internal surface area of such a system is very large. The solid forming the framework is silica, usually considered to be amorphous, although there is now some evidence to support the view that there are at least some crystalline nuclei present. It is possible that the silica is entirely present in the form of colloidal crystals—crystals so small that their existence has been overlooked in the earlier work. If the activated silica is heated for some time at temperatures of 1000°C . to 1100°C . there is an increase in the crystallinity of the substance and at the same time the capillary volume is apparently greatly reduced.

Relation of Water Content to "Activity." A fact frequently overlooked in discussions of activated silica is that the product nearly always, if not always, contains small amounts of water. This water may vary considerably in amount with the method of preparation of the gel, but its removal beyond a given point is accompanied by a great decrease in the activity of the gel. Fells and Firth² have found that gels prepared at several different temperatures had in each case about the same water content after a final heating at 600°C . Gel initially prepared at 0°C . presented an exception for in this case the final water content was appreciably lower than that of those gels prepared at higher temperatures. This gel adsorbed water vapor more slowly than did the others and its final adsorption capacity was less.

Berl and Burkhardt³ likewise found that gels which retained the lesser amounts of water after a given final treatment adsorbed the lesser amounts of water vapor. They noted also that gels which adsorb the lesser amount of

¹ Patrick, Frazer, and Rush: *J. Phys. Chem.*, **31**, 1511 (1927).

² Fells and Firth: *J. Phys. Chem.*, **29**, 241 (1925).

³ Berl and Burkhardt: *Z. anorg. allgem. Chem.*, **171**, 102 (1928).

water vapor give the lower heats of wetting. These investigators obtained their gels of different water content by varying the concentrations of the mixtures used in their preparation.

Ray¹ prepared gels of different water contents by dehydrating samples of a given preparation at successively higher temperatures. He noticed that the water content decreased linearly with increasing temperatures of activation but failed to state at what temperatures he treated the various samples to obtain the given degree of dehydration. He investigated the relation of activity to water content by comparing the adsorptive capacities of the various samples for nitrogen peroxide. Within the range 6.8 to 4.7 percent of water the amounts of N_2O_4 adsorbed per gram of gel were nearly constant. At lower water contents, such as at 3.3 percent, there was a falling off of adsorptive capacity. Ray also found evidence (unfortunately indirect) to indicate that the N_2O_4 reacted with the gel water to form HNO_3 and N_2O_3 , the HNO_3 remaining in the gel in place of the water that was originally present. The adsorptive capacity of the gel was only slightly diminished by this replacement.

McGavack and Patrick² likewise found that the adsorption of a water soluble gas (SO_2) by silica gel was not affected by changing the water content between the limits of about 5 to 8 percent, but Patrick and Davidheiser³ found that even small differences in water content produced large variations in the adsorptive capacity of silica gel for NH_3 .

Manner of Retention of the Bound Water. The investigations cited above, though dealing with the amount of water in activated silica, have contributed but little in answer to the question as to how such water is retained. There appear to be three possible ways in which this bound water may be held in the gel. (1) The water may be condensed in very fine capillary spaces. (2) It may be adsorbed as a continuous film over the surface of the solid silica. (3) It may constitute an integral part of the gel framework, even to the point of being present in chemical combination.

Jones⁴ expressed the view that the last 6 to 8 percent of the water is held in such fine capillary spaces that when it is driven out, the voids so formed cannot be occupied by molecules of other adsorbates. He based this conclusion on the fact that each of different gels with water contents of from 6.2 to 3.4 percent adsorbed the same amounts of acetic acid from a given acetic acid-gasoline solution. At a water content of one percent, he found, however, that the adsorptive capacity was much less than in the other samples. This he attributed to a breakdown of the gel structure at the high temperature necessary to dehydrate so completely.

The view that the water is adsorbed as a continuous film over the solid framework of the gel has at times received support. Patrick and Grimm⁵ in

¹ Ray: J. Phys. Chem., **29**, 74 (1925).

² McGavack and Patrick: J. Am. Chem. Soc., **42**, 946 (1920).

³ Patrick and Davidheiser: J. Am. Chem. Soc., **44**, 1 (1922).

⁴ Jones: loc. cit.

⁵ Patrick and Grimm: J. Am. Chem. Soc., **43**, 2144 (1921).

their work on the heat of wetting of silica gel assumed that the gel particles actually presented a water surface to their surroundings. With this assumption they were able to make calculations of the area of the water surface which was exposed to the wetting liquids. Using the heats of wetting of water, benzene, carbon tetrachloride and aniline they obtained values for the specific area that showed good agreement. The heat of wetting of silica by alcohol was found to be higher than that by water. To explain this fact the authors proposed the theory that alcohol is insoluble in the gel water because of the highly concave meniscus of the water which was held in the fine capillary spaces, and that a water-alcohol interface is formed. To postulate such an abnormal behavior of water toward one liquid immediately after using the normal value of its interfacial tensions against other liquids is so inconsistent that the attempt to explain the heat of wetting phenomena on the basis of the exposure of a water surface by the gel seems scarcely justified.

As a third possibility it may be postulated that the water forms an integral part of the gel framework. This would amount essentially to chemical combination of the water with the silica, differing from chemical combination as we ordinarily think of it in that stoichiometric proportions are not involved. Water molecules would be thought of as forming connecting links between particles of the solid so that when they are finally removed the structure would collapse. There has been no experimental evidence for such a view except the fact that the adsorptive capacity and the heat of wetting are greatly decreased if all the water is driven from the gel.

Summarizing, it may be stated that the evidence from the literature concerning the manner in which water is contained in activated silica is far from conclusive. Gel that is active probably always contains some water but there are decided differences of opinion both as to how this water is retained and as to the relation of the water content to the activity of the gel.

The purposes of the present investigation, then, were (1) to determine the conditions necessary for activating silica reproducibly to any desired degree, (2) to determine the relation of the amount of water in silica gel to its activity, (3) to obtain data that will indicate the manner of retention of water in the gel, and (4) to throw further light on the subject of the structure of silica gel.

The method employed in attacking these problems was to study the interrelations between temperature of activation, time of activation, water content of the resulting product, and its heat of wetting. The heat of wetting values of a series of gels were taken as representing their relative activities. The wetting agent in all the cases reported in this paper was water but an extensive series of measurements (as yet unpublished) has shown that the ratio of heats of wetting of one sample of gel by different liquids is the same as the ratio of heats of wetting of any other gel by those liquids, irrespective of differences in activity or in method of preparation of the gel. Thus, the same *relative* activities would have been obtained had any other liquid which wets silica completely been substituted for water in these experiments, and the same conclusions would have been drawn.

Experimental

Apparatus. With but one change, the calorimeter used, Fig. 1, was the same as described by Bartell and Fu.¹ A rotating propeller was used as a stirrer in place of the ring stirrer described by them. The calorimeter vessel was a Dewar flask of about 150 cc. capacity, fitted with a ground glass stopper. Through this stopper was passed a Beckmann thermometer, the mercury sealed stirrer shaft, a small heating coil, and the holder for the bulbs of powder to be used. The calorimeter was placed in an air bath, the temperature of which could be regulated to $\pm 0.05^\circ\text{C}$.

The method of operation was as follows: Approximately 60 cc. of the liquid to be used was placed in the calorimeter vessel, a small thin-walled bulb containing the sample of silica was sealed to the holder which extended through the cover, the apparatus was assembled, and the stirrer started. When the calorimeter was at the temperature of the air bath, as evidenced by constant readings of the thermometer for at least thirty minutes, a small measured current was sent through the heating coil for a known length of time, the time being determined with a stop watch. The temperature rise was noted and the heat capacity, C_p , of the entire assembly calculated in calories per degree, using the formula:

$$C_p = \frac{i^2 r t}{T J}$$

i represents the current, measured by a calibrated milliammeter; r , the resistance of the coil; t , the time; T , the temperature rise, and J , the mechanical equivalent of heat.

The apparatus was next allowed to cool to the temperature of the bath, and the bulb containing the powder was broken by gently pushing it against the side or bottom of the vessel. When the powder was wet by the liquid the temperature increase was again noted, and the heat of wetting calculated in calories per gm. from the equation:

$$-Q = \frac{T}{W} C_p$$

W represents the weight of the sample.

The heat capacity of the calorimeter plus its contents was always re-determined after the temperature rise due to wetting had been measured and the average of the two (or more) determinations was used as the C_p value in the above equation.

By suitably choosing the time interval used in determining the heat capacity, the temperature rise in the calibration could be made approximately the same as that occurring in the determination, thus minimizing the heat radiation error. In every case the full heat effect was developed in less than two minutes. Preliminary measurements were made to demonstrate that the determined heat capacity was constant throughout a considerable range of energy input, and that the temperature rise occasioned by the wetting of

¹ Bartell and Fu: Colloid Annual, 7, 135 (1929).

silica was directly proportional to the weight of the sample throughout a range of weights considerably greater than those finally used and reported. In a large number of determinations of the heat of wetting, the average deviation was ± 0.15 calories per gram.

Materials. The silica used was prepared according to the direction of Bartell and Fu. A good grade of water glass was diluted to a specific gravity of 1.025, and neutralized with 1:1 HCl. Before the mixture had set to a gel, saturated nickel nitrate solution was added in the proportion of 200 cc.

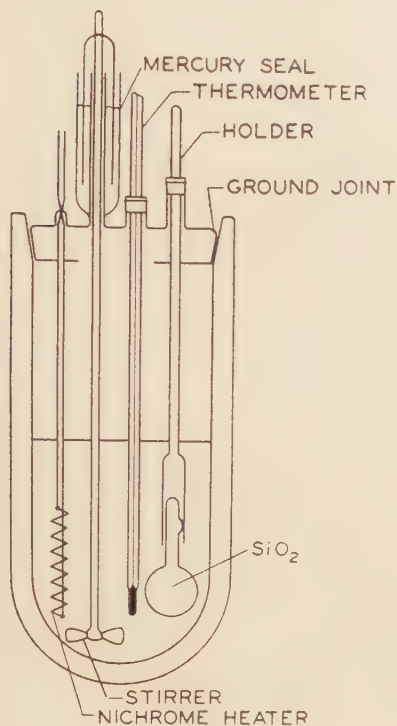


FIG. 1

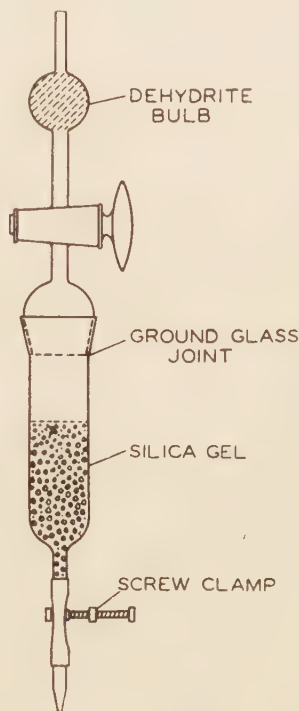


FIG. 2

nickel nitrate to 1,000 cc. of silicic acid solution. The mixture very soon set to a solid green gel, and was allowed to synerize at 90°C . for several days. When the gel appeared to be thoroughly dried it was washed with water and HCl until the wash water no longer tested for Ni^{++} with dimethyl glyoxime reagent. It was then heated at 250° in a quartz vessel for two hours and poured immediately into cold conductivity water. This last treatment, which was repeated several times, caused the larger granules to split apart and aided in removing the remaining traces of HCl. The gel was then ground and sifted, the portion having particle sizes from 40 to 160 mesh being retained. This portion was again thoroughly washed, and was finally dried at 250°C . A quantity of this gel sufficient for all our experiments was prepared and thoroughly mixed. It was stored in open vessels in a CaCl_2 desiccator at 25°C . to insure uniformity of water content before the activation treatment.

The samples of gel were activated by heating in a muffle furnace to the desired temperature for a definite length of time, and were then immediately transferred to the previously dried apparatus sketched in Fig. 2. After the transfer the small calorimeter bulbs were filled rapidly through the small opening at the lower end of the device and were sealed off at once. In every case the filling of the bulbs was completed before the gel had cooled to room temperature.

The analysis for water was made by determining the loss on ignition. When the calorimeter bulbs were being filled a larger sample was also drawn off and sealed into a test tube. After it had cooled to room temperature this sample was transferred to a platinum crucible and weighed. The crucible and the contents were then ignited to constant weight. This required heating at least six hours under a bench muffle equipped with a Meker burner having an auxiliary air blast. The crucible was always placed in a dried stoppered bottle to be weighed, since otherwise the silica gained weight too rapidly on the balance pan to permit of accurate weighing.

Conductivity water was used throughout this investigation.

Measurements and Results. If reproducible heats of wetting are to be obtained it is essential that the conditions of activation be carefully controlled. Data showing the necessity of such control are given in Table I. The furnace was heated to the temperature shown in the first column and a crucible containing approximately twenty grams of the gel placed therein. The sample was removed at the end of the time shown in the second column. In the third column the heats of wetting of the various samples are given. It must not be overlooked that an appreciable time is required to heat the sample of gel and that the time shown in the table does not represent the time at which the sample was actually at the given temperature. In general, increasing either the temperature or the time of the heat treatment decreases the activ-

TABLE I
Heat of Wetting as related to Temperature and Time of Activation

Temp. °C.	Time min.	-Q _w cal./gm.
800	15	14.87
825	10	13.61
900	15	13.13
900	30	11.98
930	10	11.98
1000	1	16.41
1000	2	13.97
1000	3	13.50
1000	4	11.63
1000	5	11.66
1000	7	11.49
1000	15	11.53

ity of the gel. This indicates that possibly the water content of the gel is an important factor in determining its activity. The next series of experiments was designed to test this view.

The temperature of activation was kept constant at 220°C . and the time of heating was varied. The water content and heat of wetting corresponding to each treatment was measured. The same procedure was followed at 500° and 800°C . The results obtained are tabulated in Table II, and plotted in Figs. 3 and 4.

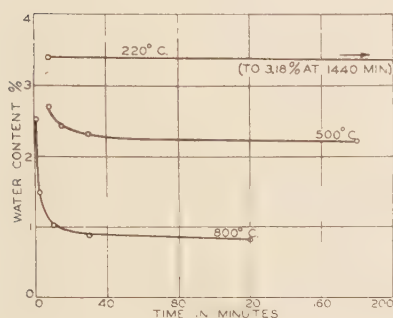


FIG. 3
Relation of Water Content to
Time of Activation.

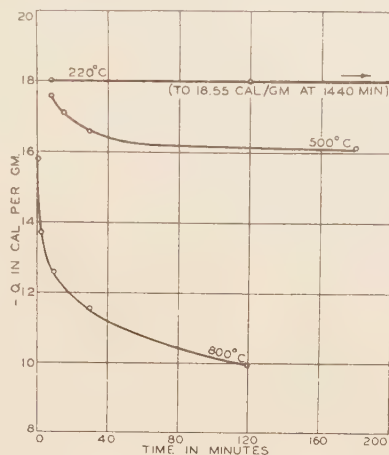


FIG. 4
Relation of Heat of Wetting to
Time of Activation.

TABLE II
Heat of Wetting and Water Content as related to Temperature and
Time of Activation

Temp. $^{\circ}\text{C}$.	Time	Water %	$-Q_w$ cal./gm.
220° *	24 hrs.	3.18	18.55
220	8 min.	3.40	18.02
235	120 "	—	18.02
500	8 "	2.70	17.59
500	15 "	2.43	17.11
500	30 "	2.32	16.60
500	180 "	2.22	16.16
800	1 "	2.54	15.80
800	2.5 "	1.50	13.72
800	10 "	1.02	12.60
800	30 "	.89	11.55
800	120 "	.83	9.97

* Under high vacuum.

Finally, a series of measurements was made at constant time of activation (2 hours) varying the temperature and again measuring both the water content and heat of wetting. The results are collected in Table III and plotted in Figs 5 and 6.

TABLE III

Heat of Wetting and Water Content as related to Temperature of Activation

Temp. °C.	Time min.	Water %	$-Q_w$ cal./gm.
140	120	3.62	17.58
235	120	—	18.02
310	120	3.12	18.23
425	120	2.54	17.46
500	120	2.24*	16.18*
620	120	1.54	15.02
750	120	—	11.59
800	120	.83	9.97

* Values interpolated from Figs. 3 and 4.

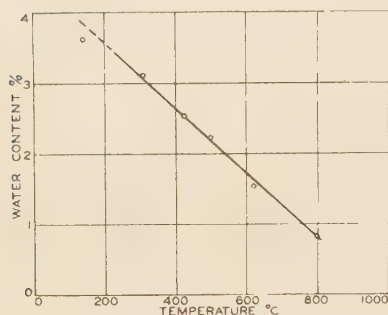


FIG. 5

Relation of Water Content to Temperature of Activation (Time of Activation = 2 hours.)

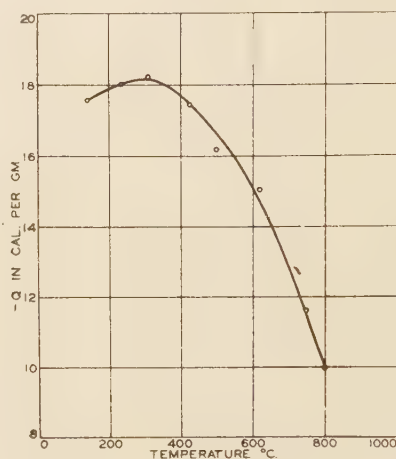


FIG. 6

Relation of Heat of Wetting to Temperature of Activation (Time of Activation = 2 hours.)

Discussion of Results

Reproducibility of Activation. The foregoing data indicate that in order to activate silica gel reproducibly, the attendant conditions must be carefully regulated. For the particular gel used in our experiments the maximum activity was obtained by heating at approximately 300° C. for a period of two hours. The activity of the product was found to be dependent upon the temperature of activation but at the lower temperatures (up to about 500°C.) the time length of treatment was of minor importance. It was also found that for at least one temperature (220°C.) the activity is not affected appreciably by heating for as long as twenty-four hours under pressure which was for periods of time as low as 5 μ and at no time was allowed to rise above one mm. of mercury.

At high temperatures the time factor in activation becomes of nearly equal importance with the temperature factor. Thus, at 800°C. the heat of

wetting per gram was lowered more than 1.5 calories when the time of activation was increased from 30 minutes to two hours. At 500°C., on the other hand, the decrease in heat of wetting per gram was only 0.4 calories when the time of activation was increased from 30 minutes to three hours. With constant time of heating, as for example a two hour period, the drop in the value of heat of wetting for a given difference in temperature of activation was much greater in the high temperature range than in the lower. Thus, between the temperatures of 750°C. and 800°C. the decrease in heat of wetting per gram was over 1.5 calories for this 50 degree change in activation temperature, while between 310°C. and 425°C. the heat of wetting was lowered less than 0.9 calories per gram for the 115 degree change in activation temperature.

In order to activate successive samples of a given gel to the same degree, the activation temperature should be kept rather low and regulated to within about 10 degrees. The time of heating should be not less than 30 minutes, in order to insure heating the sample to the same temperature throughout. The heating may be prolonged beyond this minimum time limit but no gain in the activity of the product will result. This fact makes it unnecessary to exercise special care to heat for a definite time interval.

Water in Activated Silica. It must be kept in mind that when we speak of dehydrating or of sintering silica gel to produce activated silica that we do not mean complete dehydration. Adsorptive silica appears always to contain some water, and it is with the relation of this water to activity and the manner of its retention by the gel that the remainder of this discussion will be concerned. A consideration of Fig. 7 makes immediately obvious the fact that the water content alone will not determine the activity of a gel even though the various samples are all taken from the same initial preparation. The temperature and time of dehydration are factors of equal importance with water content in determining activity. Were one to compare samples of activated silica from gels prepared in entirely different manners the divergence from a simple relationship between water content and heat of wetting would be even more striking. If the discussion be limited to a single preparation of gel such as was used in obtaining the data plotted in Fig. 7 it is seen that only one limiting condition need be imposed upon the activation treatment in order to obtain a definite relation between water content and heat of wetting. For example if it be specified that the dehydration shall be carried out in a furnace that is kept at 800°C. the relation between water content and heat of wetting, $-Q$, is shown by the plot given by the points x x x; when the de-

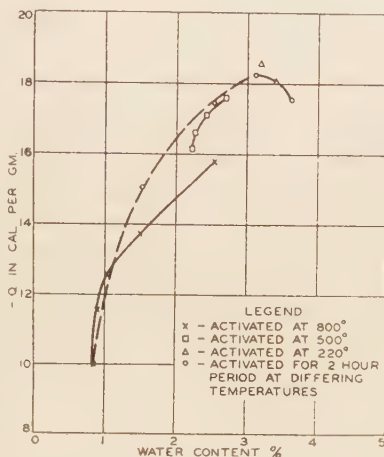


FIG. 7
Relation of Heat of Wetting
to Water Content.

hydration temperature is 500°C . the short curve through the points $\square \square \square$ is obtained. If it is specified that the time of activation of each sample be two hours, differences in water content being obtained by varying the temperature, the points on the water content-heat of wetting curve fall as indicated by the markings $\circ \circ \circ$ and the curve is the broken line passing through a maximum at approximately 3.25% water. Though it seems necessary that an activated gel contain water, the water content is not solely the determining factor of activity. At low temperatures of activation it is found that the activity increases with a decreasing water content. At high temperatures the activity decreases with decreasing water content. At 800°C . it was found that the activity decreased markedly when the time of heating was prolonged while the water content remained practically constant.

There are still several unanswered questions concerning the water which is bound in silica gel. We have seen that it is not related in a simple fashion to the activity of the product. Why, then, cannot the water be removed without greatly reducing the activity? Is the water present because the gel is active or is the gel active because the water is present? What manner of forces are responsible for the retention of the water in the gel? The data shown graphically in Figs. 3 to 7 will help us at least partially to answer these questions.

To simplify the problem let us consider that the water retained in silica gel is held in two different ways. Consider firstly that portion of the water which is easily removed. It is found that when this water is removed in successive steps the heat of wetting of the resulting gel increases. It can quite safely be assumed that this is capillary held water and that, by driving it out, the exposed surface of the silica becomes much greater. The vapor pressure of the water in very fine pores decreases rapidly as the radii of the pores decrease. At any given temperature, all the capillary spaces with effective radii above a certain minimum size will be swept free of water.

Consider secondly that water which is not easily removed. This water we shall designate as "bound" water. Much of this water persists within the gel at temperatures well above the critical temperature of water and, instead of being able to increase the apparent surface of the gel by its removal, we find that the heat of wetting decreases rapidly as this water is driven out. It is with the forces holding this bound water in the gel that we are immediately concerned.

We can at once rule out the theory of an adsorbed continuous film over the surface of the solid. In the first place the amount of water present in the gel is insufficient to produce even a monomolecular layer over a surface as great as we know is exposed by the silica. In the second place it is believed that removal of such a layer of water should tend to increase the heat of wetting when the solid, with its now unsaturated adsorptive forces, is immersed in water. We find experimentally, however, that the heat of wetting is decreased.

This decrease in activity is frequently explained as being due to "incipient fusion" of the solid particles with a resultant decrease in the surface area.

By "incipient fusion" is meant a partial fusion at temperatures below the normal melting point, made possible by the fact that the melting point of small particles is lower than that of large ones. It is scarcely credible that such an explanation (when referred to fusion in the sense in which this term is generally used) is sufficiently complete in the light of the fact that the decrease in activity is apparent in samples that have not been heated above 400°C .—more than 1000° below the normal melting point of the solid.

The fact that the water content-temperature of activation curve (Fig. 5) shows no irregularity at the point corresponding to the inversion point of the heat of wetting-temperature of activation curve (Fig. 6) would indicate that there is no difference in kind between the forces holding the bound water and those holding the easily removed water. There is, however, one objection to such a view. If the bound water is simply held by capillary forces in extraordinarily fine pores, one should expect that, once it is removed by vigorous activation treatment, these same pores would be refilled with the evolution of heat when the solid is immersed in water. It is evident that if we are to think of the bound water as held in capillary tubes, these tubes must, for some reason, collapse when the water is removed.

Were we to think of the bound water as forming, in some manner, part of the interlacing mass of threads the above objection would be overcome. The water molecules, forming connecting links between solid particles of silica would not have the properties of liquid water but would behave more like a solid. Hence, one might account for the stability of this water at temperatures above the critical temperature of water. On the other hand such links would constitute the weak points in the gel framework and when the temperature was elevated sufficiently these connecting water molecules would be driven out and the structure either would collapse or the adjacent silica particles would cohere. This would explain the decrease in internal surface with the removal of water at temperatures far below those at which we could reasonably expect fusion of fine particles of silica. It is significant that in the temperature range where this type of dehydration first begins (between 300°C . and 500°C .) the activity decreases very little with prolonged heating just as does the water content (Figs. 3 and 4). At higher temperatures (e.g. 800°C .) the activity continues to decrease with time of heating although the water content quickly attains a definite value which remains practically constant. This can be explained by assuming that the smallest particles of solid silica have acquired sufficient mobility at that temperature to undergo aggregate crystallization or rearrangement so as to fill or block off part of the capillary spaces, thus rather rapidly cutting down the effective internal surface area.

The theories that water is held structurally and that water is held by capillary forces, which theories have been offered as explanations of the retention of bound water, may be shown to be not very different if there is kept in mind the one essential fact that in extremely minute capillary spaces the usual laws of capillarity lose their validity. In larger capillary tubes the nature of the wall material does not enter into the computation of the capillary forces. For example, the height to which a liquid will rise in such a tube depends only

upon the radius of the capillary and is the same, whether the tube be of pyrex, quartz, soft glass, lead glass, or other material, so long as the liquid wets the wall material completely (i.e. forms a zero contact angle). In pores approximating molecular dimensions the properties of the wall exert a considerable influence on the behavior of a liquid within the pores. Terzaghi¹ has pointed out this fact in connection with his work on the plasticity of clays. When a liquid is held between solid particles that are only a few molecular diameters apart, he contends that it is in a "zone of forced vibrations." Under such conditions the liquid molecules lose much of their freedom of kinetic motion and assume more nearly the amplitude and frequency of vibration of the molecules forming the walls. When a silica gel is freshly formed there must be many points at which particles of solid come in contact. Near each point of contact there may be a region in which the solid walls are so close together that the water between them is in a "zone of forced vibrations." At greater distances from the points of actual contact between solid particles, the spaces are large enough to exhibit the usual capillary effects.

In the initial stages of drying it is the water in the larger capillary spaces that escapes and there is no noticeable change in the amount held in the so-called "zones of forced vibrations." As the gel shrinks on drying, the number of these smallest capillary spaces probably increases somewhat but the only change noticed is the decrease in effective internal volume. The final dried product, before activation, would consist then of solid silica particles holding very firmly a small amount of water which may be thought of either as structurally bound in the framework or as held in such fine capillary spaces that it is practically "solid water" and, in addition, some water filling the larger capillary spaces, held there by the forces ordinarily accompanying capillary condensation. Gentle activation treatment drives out this water, increasing the internal volume and internal surface area of the sample. When the bound water is removed, however, the surfaces of the solid particles are so close together that the surface forces which originally operated as forces of adhesion, holding water molecules in the pores, now function as forces of cohesion which tend to pull the walls of the capillaries together and thus to decrease the internal volume of the gel. Finally, at very high temperatures, aggregate crystallization occurs so rapidly that the gel loses its activity when held at such temperatures even though no water actually escapes from the gel mass.

It should be kept in mind that all silica gels are unstable and that all the changes mentioned above should occur, even tho slowly, at all temperatures. For example, it is known that over a period of years the activity of a gel decreases, even at room temperatures. This is probably due to this same phenomenon of aggregate crystallization which is speeded up at high temperatures until it becomes the predominating effect. It is our view then that in the lowest temperature range of activation the principal effect noticed is the sweeping out of capillary spaces with an attendant increase in internal sur-

¹ Terzaghi: *J. Rheol.*, **2**, 253 (1931).

face area. At somewhat higher temperatures the collapse of the gel structure due to the removal of "bound" water is the most noticeable effect. Finally, at much higher temperatures, the effects of aggregate crystallization are predominant. The absence of any sharp breaks in the curves (Figs. 3 to 7) is evidence that the change from one effect to the other is gradual as the temperature of activation is raised and therefore that there is no definite temperature at which one influence ceases to operate and another begins. There is merely a change in the relative effectiveness of the three influences as the temperature of activation is changed.

Summary

1. A brief review is given of the literature relating to the structure of activated silica gel, its water content and the temperature of activation. The theories bearing upon these topics are conflicting.

2. Using the heats of wetting by water as a measure of activity, the conditions under which silica may be activated reproducibly were determined. It was found that the activation temperature must be carefully controlled if successive portions of the gel are to be activated to the same extent.

For maximum activity this temperature should be in the neighborhood of 300°C . The length of time of heating is immaterial provided a minimum of thirty minutes is observed. Reducing the pressure while heating seems to have no appreciable effect.

3. The inter-relation of water content, heat of wetting (activity), temperature of activation, and time of activation were studied. From the results certain conclusions concerning the structure of activated silica, especially with reference to its water content, were drawn. It was shown that the water present in a gel before activation is not all held in the same manner. Part of it is held in comparatively large capillary spaces. This part is removed easily by gentle activation treatment and the activity of the silica is thereby increased. The remainder is held much more firmly, apparently in such fine capillary spaces that the retaining forces are those of adhesion rather than those of cohesion. When this water is removed from the gel, the gel structure seems to partially collapse, decreasing the internal volume (i.e. the effective surface) and the activity.

4. It is believed that at very high temperatures aggregate crystallization occurs, thus greatly decreasing the activity of the gel.

A STUDY OF ENERGIES OF IMMERSION OF SILICA IN A SERIES OF LIQUIDS

Introduction

The determination of the surface energy of solid-air and of solid-liquid interfacial systems constitutes a problem of outstanding importance to colloid chemistry. The problem has received a great deal of attention, but to date no reliable values for the surface energy of either of these classes of systems have been obtained. It is possible, however, to approach the problem of the energy relation at solid surfaces from the standpoint of energy changes occurring at such surfaces. When a solid is immersed in a liquid the original solid-air interface is replaced by a solid-liquid interface and an energy change occurs. This energy change, which may be called the energy of immersion, has been investigated in several different ways and values for such changes have been obtained. For the sake of clarity, a discussion of the energy changes may be divided into considerations of free surface energy changes and total surface energy changes.

Free Surface Energy Changes

When a solid is immersed in a liquid the solid-air interface disappears and an equal area of the interface solid-liquid results. We may designate the surface tension of the solid by the symbol S_1 and the interfacial tension between solid and liquid by S_{12} , and since the surface tension and the interfacial tension are equal numerically to the free surface energies of the systems solid-air and solid-liquid respectively, the free energy change per unit area upon immersion is represented by the expression, $S_1 - S_{12}$. This expression, however, is the same as that which has received treatment under the heading of "Adhesion Tension." Numerically, the adhesion tension, A_{12} , of a system represents the difference between the surface tension of a solid and the interfacial tension of the solid against a given liquid, that is, $S_1 - S_{12} = A_{12}$. The adhesion tension of a solid-liquid system may be readily evaluated if the liquid forms a contact angle with the solid. The existing relation is given by the equation of Thomas Young:³

$$S_1 - S_{12} = S_2 \cos \theta.$$

If the surface tension of the liquid is known, it is necessary to determine only the contact angle which the liquid forms with the solid, when at equilibrium, in order to calculate the adhesion tension which in turn should be numerically

¹ The material presented in this paper is from a dissertation submitted by E. G. Almy to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, February 1932.

² Holder of du Pont Fellowship, 1930-31.

³ Thomas Young: Phil. Trans., **1805**, 84.

equal to the free energy of immersion. One of the objects of the present paper is to show that the adhesion tension as determined by measurement of contact angles is in fact equal to free energy of immersion as calculated from heat of wetting data. Any of several methods may be used in measuring the contact angles to be used in calculating adhesion tension. A discussion of the various methods used for determining contact angles is to be published shortly in a paper from this laboratory. Such methods will not, therefore, be discussed in this paper.

Direct measurements of the free energy change upon immersion have been attempted by Tangl¹ and by Röntgen,² the method in each case being based upon a determination of the deformation of a film of the solid (such as a rubber membrane) when it was coated with the liquid. Such a method is applicable to liquids that form zero contact angles with the solids as well as to those that form finite contact angles. This method has two very serious defects: (1) The number of solids that can be obtained in the form of suitable membranes is very limited, and, (2) the measurements are very inaccurate.

The displacement pressure method for the measurement of adhesion tension of contact angle liquids has been extended to include the measurement of adhesion tensions of liquids which form zero contact angles with the solid. By this means the adhesion tensions of a fairly large number of solid-liquid systems have been determined. In this work it was necessary that the solid to be studied be one that could be reduced to powder. The method involves the determination of solid-liquid-air contact angles and of solid-liquid-liquid interfacial contact angles by means of displacement pressure measurements. A detailed description of the method and of the calculation employed is to be found in recent literature.

Total Surface Energy Changes

The total energy of immersion, the change in total energy which occurs when a solid-air interface is replaced by a solid-liquid interface, may be determined by measuring the heat of wetting. If E_1 be taken to represent the total energy per unit area of the solid-air interface and E_{12} , the total energy of the solid-liquid interfaces, the expression, $E_1 - E_{12}$, will represent the total energy of immersion. The relation between the free and total surface energies is given by an equation of the Gibbs-Helmholtz type,

$$E = S - TdS/dt$$

the second term of the right hand member representing the latent energy of the system.

The heats of wetting of various substances have been investigated and recorded by several authors who have not attempted to calculate the surface energy changes involved. Herbst³ has tried to correlate the heats of wetting of certain active charcoals with their various physical properties. Kobayashi

¹ Tangl: Ann. Physik, (4) **34**, 311 (1911).

² Röntgen: Wied. Ann., **3**, 324 (1878).

³ Herbst: Kolloid-Z., **38**, 314 (1926).

and Yamamoto¹ have utilized this quantity in estimating the relative surface areas of adsorbent clays. Bouyoucos² has used the heat of wetting as a means of estimating the colloid content of soils. The large specific surface of colloids assures that the amount of colloids in soils is approximately proportional to the heat of wetting. Grimm, Raudenbusch, and Wolff³ have compared the heats of wetting of silica gel by various liquids with the preferential adsorption of those liquids by the gel, particularly as it might apply to the separation of binary liquid mixtures by silica. Landt⁴ has used heat of wetting data as a means of estimating the relative surface areas of adsorptive carbons.

A few researches have been conducted in which attempts have been made to calculate surface energy changes. It has been pointed out⁵ that no matter what the mechanism of wetting, the heat developed is a measure of the decrease in total surface energy when the solid-air interface is replaced by a solid-liquid interface. Using the microscope to determine the specific surface of the powder, Harkins and Dahlstrom⁶ were able to estimate the energy of immersion per sq. cm. of crystalline TiO_2 in each of several liquids from heat of wetting data. Inasmuch as they believed that the microscopic method gave too small an area, they arbitrarily multiplied the measured specific area by two. They do not fully justify the choice of this particular factor and, as a result, the absolute magnitudes of their calculated energies can hardly be considered to be exact. The relative values of their energies of immersion are probably correct. Koehler and Mathews⁷ found the heat of wetting of PbSO_4 by water to be less than their experimental error. They had estimated the area of the solid by a radioactive indicator method and so were able to conclude that the decrease in total surface energy when dry PbSO_4 is wet by water is less than 71 ergs/cm². Patrick and Grimm⁸ determined the heats of wetting, by each of several liquids, of silica gel containing water. They assumed that such a gel presented an all water surface to the wetting liquid and, on that basis, calculated the area of surface so exposed. For several liquids they obtained good agreement of area, but they were unable to explain satisfactorily the high heats of wetting of water miscible liquids.

Bartell and Fu⁹ have shown that, with the aid of certain assumptions, it is possible to relate adhesion tension to the total energy change per sq. cm. when a solid is immersed in a liquid. This treatment permits of the estimation of the specific surface area of the solid from heat of wetting data and, in consequence, makes possible the determination of the energy relations at the solid-liquid interface for those liquids that cannot be studied by the displace-

¹ Kobayashi and Yamamoto: *J. Soc. Chem. Ind. Japan*, **31**, 434 (1928).

² Bouyoucos: *Soil Science*, **19**, 153 (1925).

³ Grimm, Raudenbusch, and Wolff: *Z. angew. Chem.*, **41**, 104 (1928).

⁴ Landt: *Z. Vereins. deutsch. Zucker Ind.*, **79**, 44 (1929).

⁵ Bartell and Fu: *Colloid Annual*, **7**, 135 (1920).

⁶ Harkins and Dahlstrom: *Ind. Eng. Chem.*, **22**, 897 (1930).

⁷ Koehler and Mathews: *J. Am. Chem. Soc.*, **46**, 1158 (1924).

⁸ Patrick and Grimm: *J. Am. Chem. Soc.*, **43**, 2144 (1921).

⁹ Bartell and Fu: *loc. cit.*

ment pressure method (water miscible liquids). In their preliminary measurements, these investigators found good agreement between the theory and the experimental values obtained.

It is with this relation between adhesion tension, which should be numerically equal to the free energy of immersion, and the total energy of immersion as measured by the heat of wetting, that this paper is primarily concerned. It is essential to the development of the mathematical relation between these quantities that the heats of wetting of two different samples of silica by any one liquid be proportional to the surface area of the two samples. A survey of the literature on heats of wetting of silica gel would indicate that the values of heats of wetting by the same liquid are very different for different samples of gel and that the heats of wetting of one gel by a series of liquids bear no definite relation to the heats of wetting of another gel by the same series of liquids. The first of these differences is easily explained by assuming that the gels used by different investigators presented different specific surface areas. We had reason to believe, however, that if the heats of wetting of one silica gel by each of two liquids stood in a certain ratio, the heats of wetting of another sample of silica by the same two liquids should stand in the same ratio and that the disagreement in such relative values found in data from the literature was due to experimental error of one kind or another. The first object, then, in the present investigation was to compare the heats of wetting of various preparations of silica by several liquids to determine whether or not the ratio of the heats of wetting of the gel by liquid A and by liquid B is the same for all samples of silica.

If such a constancy of ratios is found it may be concluded that the relative heats of wetting represent very closely the relative total energies of immersion. We have already indicated that total energies of immersion can also be calculated from adhesion tension data. These values can then be reduced to a relative basis and a comparison made between the relative total energies measured by heats of wetting and relative total energies calculated from adhesion tension data. Agreement between the two sets of values would indicate that the adhesion tension values represent free energies of immersion and that it is possible to calculate free energies of immersion from total energies of immersion, or the reverse, i.e., it is possible to calculate total energies of immersion from free energy of immersion data obtained from adhesion tension measurements.

Experimental

Apparatus: The calorimeter used and the procedure followed in the heat of wetting determinations have been described in an earlier paper.¹

Materials: Silica gel prepared as described in the earlier paper was used in this investigation and designated as Silica A.

Silica B was a commercial silica gel which was refluxed with nitric acid for several hours and then washed until free from acid. It was a harder gel than Silica A and seemed to be more active.

¹ Bartell and Almy: J. Phys. Chem., **36**, 475 (1932).

Silica C was prepared by neutralizing sodium silicate (specific gravity 1.025) with hydrochloric acid (1:1). After the mixture had set to a gel it was placed in a refrigerator at $-15^{\circ}\text{C}.$, and allowed to stand for forty-eight hours. This freezing process broke down the gel as surely and much more rapidly than slow drying, so that upon thawing, the active silica could readily be washed free from salts and acid. The product was very soft and could be crushed to a powder easily. Its activity was about the same as that of Silica B.

The liquids used were carefully purified to insure the absence of capillary active substances.

Water: Conductivity water was used throughout.

Nitrobenzene: The nitrobenzene was washed with acid and dried over K_2CO_3 . It was then distilled with steam and redistilled in vacuo. It was then fractionated at atmospheric pressure, the portion boiling at $210.9 \pm .1^{\circ}\text{C}.$ being retained. Finally it was recrystallized twice. The freezing point was $5.60 \pm .02^{\circ}\text{C}.$ It was stored in a flask that contained a tube of P_2O_5 .

Benzene: Baker's C. P. Benzene was washed with acid and with alkali and refluxed over successive portions of mercury until the surface of the latter remained bright. It was then fractionally crystallized, the portion freezing at $5.48 \pm .02^{\circ}\text{C}.$ being retained. This was distilled from P_2O_5 to dry the product. Its boiling point was $82.20 \pm .01^{\circ}\text{C}.$

Chlorobenzene: Carefully purified chlorobenzene was used. Its boiling point was $132.01^{\circ}\text{C}.$, and its density 1.1008 at $25.13^{\circ}\text{C}.$

Ethyl Benzene: Eastman's best grade of ethyl benzene was fractionally distilled from P_2O_5 , the fraction boiling at $136.10^{\circ} - 136.13^{\circ}\text{C}.$ being retained.

Chloroform: Mallinckrodt's C. P. chloroform was found not to discolor mercury on shaking nor to precipitate with silver nitrate in water solution. It was distilled from P_2O_5 to remove any trace of alcohol or moisture, and the fraction distilling over at $61.18^{\circ}\text{C}.$ was stored in a dark-colored glass-stoppered bottle.

Carbon tetrachloride: A good grade of carbon tetrachloride was washed with sulfuric acid and with alkali, dried over fused KOH and shaken with successive portions of mercury until the surface of the latter was no longer darkened by contact with the liquid. It was finally fractionally distilled from P_2O_5 , the fraction coming over at $76.75^{\circ}\text{C}.$ being retained.

Hexane: Synthetic hexane from Eastman Kodak Co. was further purified by shaking with concentrated sulfuric acid, then with alkaline permanganate and finally with acid permanganate. It was dried over fused KOH and distilled fractionally from P_2O_5 . A middle fraction boiling at a constant temperature of $68.80^{\circ}\text{C}.$ was collected and used.

Measurements and Results:

The importance of the removal of capillary active impurities from the liquids used is made evident by the data for the heat of wetting by benzene containing varying amounts of water (Table I). It is seen that mere traces of water may raise the heat of wetting of benzene by as much as 50%. For this

reason the following precaution was observed. Just before closing the calorimeter at the beginning of each determination a small amount of activated silica was dropped into the liquid contained therein. This treatment removed any traces of moisture that may have been introduced during the transfer of the liquid to the calorimeter.

TABLE I
Heats of Wetting by Benzene containing Varying Amounts of Water

Per cent water	Heat of wetting
0.000	10.64 cal./gm.
.015	13.47
.030	14.96
.059	17.07

A series of heats of wetting by water, by nitrobenzene, and by benzene on samples of silica A of widely different water contents and activities were determined. The differences in activity and in water content were induced by varying the temperature and time of activation treatment as described in the earlier paper. The results are collected in Table II. Q_w , Q_n , and Q_b represent the heats of wetting by water, nitrobenzene, and benzene, respectively.

TABLE II
Heats of Wetting of Gels of Differing Water Contents by Water, Benzene and Nitrobenzene

$\frac{\text{Mols H}_2\text{O}}{\text{Mols SiO}_2}$	Q_w	Q_b	Q_b/Q_w	Q_n	Q_n/Q_w
0.18	13.8	—	—	10.3	.75
.15	17.0	12.1	0.71	13.4	.79
.14	17.0	11.7	.69	15.0	.88
.13	18.3	12.2	.67	14.5	.79
.11	17.9	11.2	.63	14.1	.79
.11	17.8	11.8	.65	13.9	.78
.097	19.3	12.4	.64	14.5	.75
.094	16.1	10.8	.67	13.1	.81
.089	17.2	11.2	.65	13.5	.78
.060	17.0	11.1	.65	12.5	.74
.048	14.3	9.3	.65	11.6	.81
.042	13.8	9.6	.69	11.5	.83
.019	9.4	6.3	.67	7.8	.83

Av. .66 $\pm$.02

Av. .80 $\pm$.02

It was noticed that with all these samples of silica the ratios Q_b/Q_w , and Q_n/Q_w were constant to within a few per cent, and it was deemed advisable to determine whether this same condition would prevail with other liquids and with samples of silica prepared in entirely different manners. For this reason, Silica B and Silica C were prepared as above described, and the heats of wetting by several liquids determined for samples of each of these types, and also

for another sample of Silica A. The activation treatment in each case was to heat at approximately 250°C. for three hours. Table III shows the data obtained for determining the heats of wetting, and in Table IV the results are summarized.

TABLE III
Details of Heats of Wetting Determination

Liquid	Heat Cap. of System	Wt. Sample of Gel	ΔT	$-Q$	
Silica A.					
Water	66.61	.8515	.240	18.86	
	66.82	.6706	.187	18.63	
				—	18.75
Acetone	32.88	.4541	.287	20.78	
	32.88	.5308	.336	20.82	
				—	20.80
Ethyl- Benzene	20.62	.6286	.230	10.84	
	20.76	.8497	.310	10.86	
				—	10.85
Chloroform	20.43	.6587	.234	10.45	
	20.43	.6554	.228	10.24	
				—	10.35
Silica B.					
Water	66.86	1.1920	.435	24.42	
	66.86	1.6829	.618	24.48	
				—	24.45
Acetone	33.17	.9047	.706	25.89	
Ethyl- benzene	30.47	1.0534	.478	13.83	
	31.06	.7373	.324	13.65	
				—	13.74
Chloroform	29.39	1.2332	.558	13.30	
	29.39	.7771	.350	13.24	
				—	13.27
Silica C.					
Water	66.70	.8826	.296	22.37	
	67.27	.6783	.225	22.31	
				—	22.34
Acetone	33.28	.5312	.318	23.87	
	32.42	.4963	.366	23.90	
				—	23.89
Ethyl- benzene	29.62	.6569	.267	12.04	
	29.71	.4788	.189	11.73	
	29.71	.6306	.262	12.34	
	29.58	.5859	.232	11.71	
				—	11.95
Chloroform	29.00	.5271	.214	11.77	
	29.93	.5498	.217	11.82	
				—	11.80

TABLE IV
(Summary of Table III)

Heats of Wetting of Three Silicas by Four Different Liquids

Silica. Heat of wetting by:

	Water	Acetone	Ethyl benzene	Chloroform
A	18.75	20.80	10.85	10.35
B	24.45	25.89	13.74	13.27
C	22.34	23.89	11.95	11.80

The ratios of the heats of wetting of silica A were determined for these liquids and compared with the ratios of the heats of wetting of silicas B and C. The values are shown in Table V in which the symbols not previously defined

TABLE V
Ratios of Heats of Wetting of Different Silicas by Different Liquids

Silica	Q_a/Q_w	Q_e/Q_w	Q_c/Q_w
A	1.06	0.58	0.55
B	1.11	0.54	0.54
C	<u>1.07</u>	<u>0.56</u>	<u>0.53</u>
	1.08	0.56	0.54

are Q_a , Q_e , and Q_c for heats of wetting by acetone, ethyl benzene and chloroform, respectively. Again it is observed that while the absolute values for heats of wetting may vary from one sample of silica to another, the relative values of the heats of wetting by a series of liquids are the same as we pass from one sample of silica to another even though those samples may vary widely in their physical properties, activity, and methods of preparation.

Since the ratio of heats of wetting by two liquids is then largely independent of the sample of silica used, the heats of wetting by other liquids than those already discussed may be determined on new samples of silica and reduced to a basis comparable with the others if the heats of wetting by a reference liquid, such as water, be determined for each sample of silica used. In Table VI are

TABLE VI
Heats of Wetting by Three Organic Liquids compared to Heats of Wetting by Water

Gel sample	Q_{water}	$Q_{\text{organic liquid}}$	Ratio Q_o/W_w
A ₁	18.0	11.3 Chlorobenzene	.62
A ₁	18.0	6.6 n-Hexane	.37
A ₂	16.1	7.3 Carbon tetrachloride	.45
A ₃	14.3	6.4 Carbon tetrachloride	.45

shown the heats of wetting of a few liquids for samples of silica of such activity that the heats of wetting by water are those shown in the second column. The liquids reported in this table were chosen because some of the most reliable

adhesion tension data available were obtained for these same liquids against silica. The total energies of immersion found experimentally from heats of wetting of these liquids by silica can then be compared with those calculated from the adhesion tension data available for these liquids against silica.

Discussion of Results

Ratios of Heats of Wetting of Different Gels:

It has been pointed out that the data to be found in the literature on the heats of wetting of silica gel are highly discordant as regards both absolute values and relative values. The present work has shown, however, that the relative values of the heats developed when exactly similar samples of gel are wet by a series of liquids are always the same; i.e., for any sample of silica the heat of wetting by benzene is .66 times that by water, while that by acetone is 1.08 times that by water, etc.¹ It is essential only that the samples of silica wetted by the liquids to be compared be uniform in surface area, a condition that requires careful control of experimental methods.

We can now with justification reduce the heats of wetting of silica by all the liquids studied to a comparable basis even though no one sample of silica was used throughout the entire series of liquids. Since the ratios of heats of wetting by different liquids are constant we can arbitrarily set the heat of wetting by a reference liquid equal to unity and calculate the heats of wetting by the other liquids for the same sample of silica. If benzene be chosen as the reference liquid ($-Q = 1.00$) the relative values of the heats of wetting by all the liquids are shown in Table VII. Now, if the heat of wetting of a given gel by

TABLE VII

Relative Heats of Wetting of Silica by Nine Different Liquids. (Benzene = 1)

Liquid	-Q	Liquid	-Q
Acetone	1.64	Ethyl benzene	.85
Water	1.51	Chloroform	.82
Nitrobenzene	1.21	Carbon tetrachloride	.69
Benzene	1.00	Hexane	.56
Chlorbenzene	.94		

any of the liquids in this series is known, the heat of wetting by any of the other liquids is easily calculated. It is necessary only to multiply by the appropriate conversion factor, which factor can readily be obtained from the ratio values in the table.

From the fact that the ratio of the heats of wetting of silica gel by two liquids is constant though the water content of the gel is varied, some interesting conclusions can be drawn concerning the part played by the gel water in the energy changes occurring when the gel is immersed in a liquid. This is a

¹ In the results on heats of wetting of charcoal reported by Herbst (loc. cit.) a similar effect may be noticed although he did not specifically call attention to it. An examination of his data shows that for five different samples of activated charcoal being wet by water and by benzene, the quotient Q_w/Q_b was $0.751 \pm .003$.

subject over which there has, in the past, been considerable controversy. It has been shown¹ that the water cannot be present as a continuous film, thus exposing an all-water surface to the wetting liquid. This leaves one of two alternatives, (1) the area of the water surface must be so small in comparison to the surface of the silica that it may be ignored, or (2) the gel must present a composite surface of silica and water, the proportion of solid to liquid changing as the water content changes. The following equations would seem to present sufficient evidence to justify the conclusion that the ratio of the heats of wetting of the water containing gel by two liquids is the same as the ratio of the heats of wetting of dry silica by the same two liquids.

The following expression may be used to represent the energy changes which occur when unit area of the composite surface is immersed in a liquid:

$$xa + (1-x)b = q_1$$

in which, for unit area of gel x is the area fraction of silica and $(1-x)$ is the area fraction of water surface. a and b are the energy changes which occur when the silica and water, respectively, are immersed in the liquid. q is the heat evolved. If another sample of the same gel be immersed in another liquid the analogous expression is:

$$xc + (1-x)d = q_2$$

Dividing one equation by the other we obtain:

$$\frac{xa + (1-x)b}{xc + (1-x)d} = \frac{q_1}{q_2}$$

In this expression, a , b , c , and d are fixed quantities for any pair of liquids; x may have any value from 0.0 to 1.0. But the right hand member of the equation, q_1/q_2 is the ratio of the heats of wetting of the gel by the two liquids and is the quantity which, we have seen, remains constant though the water content varies. It follows that the left hand member of the equation above must remain constant for all possible values of x . This can be true only if $a/c = b/d = q_1/q_2$. We can conclude, then, that the ratio of the heats of wetting, q_1/q_2 , of the gel, even though it contains some water, is the same as the ratio of the total energies of immersion of the dry silica, a/c . It is also evident that one of two postulates must explain the part played by the gel water. Either (1) the water must be so contained that its exposed surface area is negligibly small in comparison with the area of the solid, or (2) the ratio of energies of immersion of silica in two organic liquids has the same value as the ratio of the energies of immersion of water in the same two organic liquids.

The evidence obtained in a study of water content of activated silica¹ indicates that the first of the two postulates probably represents the actual condition within the gel. The residual water is thought to be confined in the finest of the gel micropores and to be practically surrounded by silica. The area exposed therefore should be relatively small. Evidence that the statement in the second postulate represents a general relation between organic liquids at

¹ Bartell and Almy: J. Phys. Chem., **36**, 475 (1932).

the surface of water and at the surface of a polar solid has been presented by Harkins and Dahlstrom¹ and by Bartell and Hershberger.² It follows that even though the gel should expose an appreciable area of water surface that the constancy of ratio would be observed. It is probable, however, that the first postulate is sufficient to explain the heat of wetting relationships between differing silicas and a series of liquids.

Comparison of Observed Ratios and Ratios calculated from Adhesion Tension Data:

The relation between adhesion tension and heat of wetting as developed by Bartell and Fu is expressed by the following equation:

$$-Q = a(A_{12} - KT \, dS_2/dT)$$

where a represents the area of the solid; A_{12} , the adhesion tension; S_2 , the surface tension of the liquid; K , the adhesion constant; and $-Q$, the heat of wetting. This equation can be simplified if, instead of the adhesion tension, we use the equivalent value KS_2 . We then have the expression:

$$-Q = a(KS_2 - KT \, dS_2/dT)$$

But

$$S_2 - T \, dS_2/dT = E_2, \text{ the total surface}$$

energy of the liquid and it must follow that:

$$-Q = aKE_2.$$

Thus, given the specific surface area of a sample of silica and the adhesion tension (or adhesion constant) of a liquid for the silica it is possible to calculate the heat of wetting of the solid (per gram) by the liquid.

In deriving the above equation three assumptions were implied or stated and it is now desirable that their soundness be considered. It was necessary, first, to assume that silica gel presents the same type of surface to the wetting liquid as does the mineral silica used in determining the adhesion tensions. While this point is not susceptible of direct proof the silica used in each case was of a high degree of purity and, since no reason can be advanced for believing the surface energy relations of the two silicas to be different we feel justified in proceeding under the assumption that they are the same.

A second assumption was implied in the entire derivation—namely that data obtained from the displacement pressures set up at a liquid-liquid interface in pores of silica could be compared to energy changes when silica is immersed in pure liquids. In the adhesion tension determinations it was necessary to measure the equilibrium pressure set up by a liquid-liquid interface in capillary pores of the solid and there is a possibility that mutual saturation of water and organic liquid occurs, thus causing the measured values to represent the free energy changes when saturated liquids wet the solid. Evidence that any error due to such a cause is negligible is found in the following: Bartell and Whitney (results not yet published) have called attention to the fact that the work of adhesion between silica and an organic liquid is approximately 1.10

¹ Harkins and Dahlstrom: loc. cit.

² Bartell and Hershberger: Ind. Eng. Chem., **22**, 1304 (1930).

times the work of adhesion between water and the same organic liquid and that this ratio is constant for a great many liquids. In calculating the work of adhesion between a solid and a liquid it was necessary to use the value of the adhesion tension of the liquid against the solid. If mutual saturation influences the determined values of the adhesion tensions the effect should be confined to the values for liquids which form a zero contact angle with the solid, since the determination of the adhesion tension of a liquid which forms a finite angle with the solid requires only the measurement of the pressure with which the liquid displaces air from the pores and at no time is a liquid-liquid interface used. Such a determination should be free from any error due to mutual saturation. It was found, however, that the work of adhesion ratios calculated as above for contact angle liquids agreed with the ratios found for zero contact angle liquids. Consequently it would seem that any error due to mutual saturation in the displacement pressure cells is very probably smaller than the error of the experiment.

Finally, besides the fundamental assumptions just discussed, a third assumption was necessary to transform the equation into a usable form. Thermodynamically, the development was rigorous to the point that:

$$-Q = a(A_{12} - T dA_{12}/dT)$$

Experimental data concerning the temperature coefficient of adhesion tension, dA_{12}/dT , are not available as yet but the equation was changed by Bartell and Fu into a form of which all the terms except area are known by substituting $K dS_2/dT$ for dA_{12}/dT . The substitution follows from the fact that:

$$A_{12} = S_1 - S_{12} = KS_2,$$

and therefore:

$$dA_{12}/dT = K dS_2/dT.$$

This expression is based on the assumption that K is independent of temperature, an assumption which the authors in their preliminary paper did not justify further than to state that the error so introduced, if any, must be very small. It is, however, possible to justify the assumption in a qualitative way and even to estimate the order of magnitude of the error that may be introduced thereby. At 25°C . A_{12} is K times as large as S_2 and at the critical temperature both A_{12} and S_2 become zero. It is known that the surface tension of liquids decreases in an *approximately* linear fashion as the temperature increases. Adhesion tension, measuring the decrease in free surface energy when a solid is wet by a liquid is principally dependent upon the adsorption of liquid molecules upon the solid, and such adsorption has been shown to decrease in an *approximately* linear fashion with temperature. Since both S_2 and A_{12} decrease toward the same point in an *approximately* linear manner, and since at 25°C . $A_{12} = KS_2$, it follows that at any other temperature A_{12} must be K times as large as S_2 , or, in other words, K does not vary with changing temperature.

In this justification, however, two approximations were involved and it is important that we attempt to evaluate the probable error introduced thereby.

While it is true that over short ranges of temperature dS_2/dT is practically constant, the line defined by this slope will not cross the surface tension axis of coordinates at the critical temperature. In Table VIII are shown, in the first column, values for the temperature coefficient of surface tension (dS_2/dT) taken from the literature. In the second column are shown the temperature coefficients that would be observed if the surface tension of each liquid decreased in an exactly linear fashion from its value at 25°C. to zero at its critical temperature. It is seen (column 4) that the difference between the two sets of values is not less than 19 per cent for any of the liquids and is as high as 35 per

TABLE VIII
Comparison of dS_2/dT with $S/(t_c-25)$ at 25°C

Liquid	$-dS_2/dT$ (expt.)	$-S_2/(t_c-25)$	Difference	Per cent Difference
Water	.155	.206	.051	34
Benzene	.132	.107	.025	19
Chlorobenzene	.121	.098	.023	23
Ethyl benzene	.110	.088	.022	25
Chloroform	.137	.111	.026	19
Carbon tetra-chloride	.124	.101	.023	19
Hexane	.105	.085	.020	19

cent in the case of one of them (water). If, then, the adhesion tension of the liquid against silica should decrease in an exactly linear manner to zero at the critical temperature, the deviations of $K dS_2/dT$ from the true dA_{12}/dT would be between 20 and 35 per cent. Since, however, the evidence that A_{12} decreases linearly with temperature is of such a nature that it is possible to state only that the decrease is approximately linear and since there is nothing to indicate that any deviation from an exact linear relation is in one direction or in the other, the deviation of dA_{12}/dT from $K dS_2/dT$ may be either smaller or larger than the figures given above.

Thus there is introduced into the expression connecting adhesion tension and heat of wetting a term of considerable uncertainty which will tend to throw some doubt on the absolute correctness of values calculated by use of the expression. The relative values for different liquids, however, should be approximately correct, and we feel justified in comparing relative values of heats of wetting calculated from adhesion tension data by means of this expression with the relative values actually observed. In fact they are probably within the limits of error usually involved in heat of wetting determinations.

If benzene is again used as the reference liquid, as was done in calculating the values for Table V, it will be necessary to arbitrarily choose a value for a in the expression

$$-Q = aKE_2$$

that will make $-Q$ equal to unity. When this is done and the same value of a is used to calculate the heats of wetting of silica by the other liquids the values

obtained for the heats of wetting are those shown in the fourth column of Table IX. For purposes of comparison, the relative heats of wetting observed are recorded again in the fifth column of the same table. The substantial agreement between the two sets of values is satisfactory in view of the fact that in developing the equation for obtaining the calculated values it was necessary to resort to an assumption that invalidates the absolute accuracy of the results.

There is evidence to indicate that the absolute values, as well as the relative values for a series of liquids, of the heats of wetting calculated from adhesion tension data are approximately correct. The specific surface area of silica gel

TABLE IX
Comparison of Observed and Calculated Values of Heats of Wetting

Liquid	K*	E ₂	Relative values of		On basis of a = 5×10^6	
			-Q _{calc.}	-Q _{obs.}	-Q _A [†]	-Q _R [‡]
H ₂ O	1.07	118.2	1.21	1.51	15.1	19.0
C ₆ H ₅ NO ₂	1.33	79.4	1.01	1.21	12.6	15.2
C ₆ H ₆	1.55	67.6	1.00	1.00	12.5	12.5
C ₆ H ₅ Cl	1.25	69.0	0.81	0.94	10.1	11.8
C ₆ H ₅ C ₂ H ₅	1.45	61.4	0.85	0.85	10.6	10.6
CCl ₄	1.39	63.4	0.77	0.69	9.6	8.5
C ₆ H ₁₄	1.42	49.5	0.67	0.56	8.4	7.0

K—values obtained from work of Bartell and Whitney (unpublished).

† -Q_A—calculated from adhesion tension data.

‡ -Q_R—calculated from relative values observed.

has been estimated by several investigators using different means and the values fall fairly close to 5×10^6 cm.² per gram as an average. The specific surface may vary between rather wide limits, depending upon the method of preparation and the activation treatment of the gel, but the average of the values for specific surface area as estimated by other authors should be the same as the area of some of the more highly activated gels used in the present work. The heats of wetting by the liquids in question of a gel whose specific surface area is taken arbitrarily as 5×10^6 cm.² per gram can be calculated from adhesion tension data. The values obtained by such calculation are those shown in the sixth column of Table IX. Comparison of these values with the actually obtained heats of wetting presented in Tables II, III, and VI shows at once that there can be obtained by calculation from adhesion tension data approximately correct values for heats of wetting and, therefore, for total energies of immersion. In the final column of Table IX we have shown heats of wetting by the same liquids (calculated from the observed relative heats of wetting) of an hypothetical gel whose heat of wetting by benzene coincides exactly with the calculated heat of wetting by benzene shown in the preceding column. These were included for purposes of comparison since there are not included in the previous tables, experimental values for heats of wetting of any

one sample of silica by all the liquids. It is obvious, of course, that the relative discrepancies between the figures of the last two columns are the same as those found between columns 4 and 5. Considering the nature of the calculations involved this agreement is satisfactory.

An objection has been made to the use of the displacement pressure method for measuring adhesion tensions on the ground that the solid when packed into the cell is exposed to the vapors of the liquid before wetting occurs with the result that what is measured is not the free energy of immersion of the solid surface itself in the liquid but the free energy change, which occurs when the solid coated with an adsorbed film of vapor is immersed in the liquid. Since, however, the total energy of immersion values calculated from adhesion tension data do agree so well with the values calculated from heats of wetting, it seems justifiable to conclude that the adhesion tensions so determined must represent closely the free energies of immersion of the dry powder in the liquid. That the heat of wetting represents the total energy of immersion of a solid in a liquid is also a justifiable conclusion.

Summary

1. Methods of determining the change in free surface energy when a solid-air interface is replaced by a liquid-air interface are briefly discussed.

2. A brief survey of the literature concerning attempts to relate heats of wetting to total surface energy changes is given.

3. It is found that the heats of wetting of one silica gel by a series of liquids stand in the same ratio to each other as the heats of wetting of any other silica gel by the same liquids. This is found to be true for gels varying in method of preparation, in physical properties (such as hardness), in water content and in activity.

4. It is deduced from the above relation that, even though it is known that silica gel contains small amounts of water, the heats of wetting of a gel by a series of liquids have the same relative values as the total energies of immersion of *dry* silica in the same liquids.

5. The theoretical equation relating adhesion tension to heat of wetting is discussed with especial attention to the approximations involved and the probable extent of the errors introduced by using such approximations.

6. Relative heats of wetting calculated from adhesion tension data are compared with relative heats of wetting observed experimentally and satisfactory agreement obtained.

7. Absolute heats of wetting calculated from adhesion tension data, on the basis of an assumed area for the gel, are found to agree satisfactorily with the observed heats of wetting.

8. The above facts are used to substantiate the probable correctness of the adhesion tension values as determined by displacement pressure measurements and to indicate that adhesion tension and free energy of immersion are numerically the same.

*University of Michigan,
Ann Arbor, Michigan.*

